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Description

DIESEL MOTOR FUEL ADDITIVE COMPOSITION

BACKGROUND OF INVENTION

[0001] 1. Field of the Invention

[0002] This invention relates to a diesel fuel additive composition comprising:

(a) a detergent component selected from the group consisting of (i) a reaction product component of a substituted hydrocarbon and an amino compound, and (ii) a polybutylamine or polyisobutylamine; and (b) a fuel conditioner component comprising (i) a polar oxygenated hydrocarbon compound, and (ii) an oxygenated compatibilizing agent, for use in bulk production of diesel fuels for improving performance.

[0003] 2.Description of the Related Art

[0004]

Diesel fuel impurities can arise from a variety of sources. They can form during refining or they can develop as a result of the oxidation which occurs during storage. Such impurities tend to be both soluble and insoluble materials having higher molecular weights and boiling points than the fuel, and which manifest themselves in the engine as colors or gums. Impurities can also be introduced into the fuel during handling or during storage from corrosion of storage vessels.

Impurities can even take the form of other additives intentionally introduced by the manufacturer to solve or prevent some particular problem or improve the fuel itself, such as, for example, anti-oxidants, rust preventative, etc.

- [0005] Regardless of the source, any of these impurities can cause deposits to from in the fuel system of compression ignition engines, and, in particular, in the fuel injectors. These deposits coat or adhere to injector parts and cause injector sticking, injector tip fuel metering passage fouling, nozzle hole plugging, leakage past critical surfaces, and delayed injection (and, hence, delayed start of combustion). These problems, in turn, result in significantly increased engine noise, smoke emissions, misfiring, low temperature or cold start problems, and idle roughness, and decreased power output and fuel economy.
- [0006] It is believed that these engine problems are the result of long ignition delays, significantly contributed to by deposits, causing an excessively rapid pressure rise in the cylinder once combustion does occur.

 Recent evidence suggests that the long delay provides the time for certain chemical reactions to take place in the atomized fuel charge prior to ignition, resulting in products which burn exceedingly rapidly once combustion begins, thereby causing the undesirable rapid pressure rise, and the resultant problems.
- [0007] Today's diesel engines require a clean-burning, stable fuel that is capable of performing well under a variety of operating conditions.

- [0008] It is an object of this invention to provide a diesel fuel additive for diesel fuels, which accelerates the combustion phenomenon and reduces ignition delay in diesel engines. It is a feature of this invention that the additive comprises a detergent component and a fuel conditioner component, which synergistically interact to reduce particulate emissions and increase Cetane number.
- [0009] It is a further object of this invention that the additive comprises a detergent component and a fuel conditioner component, which synergistically interact to reduce fuel consumption in diesel engines.

SUMMARY OF INVENTION

- [0010] An object of the present invention is directed to a diesel fuel additive composition that reduces particulate emissions and improves fuel economy while improving engine performance comprising a mixture of: (a) from about 10 to about 90 weight percent, based upon the total weight of the additive, of a detergent component selected from the group consisting of (i) a reaction product of: (A) a substituted hydrocarbon of the formula $R_1 X$
- [0011] wherein R_1 is a hydrocarbyl radical having a molecular weight in the range of about 150 to about 10,000, and X is selected from the group consisting of halogens, succinic anhydride and succinic dibasic acid, and (B) an amino compound of the formula $H = (NH (A)_m)_n Y R_2$ (II)

[0012] wherein Y is O or NR $_5$, R $_5$ being H or a hydrocarbyl radical having 1 -

30 carbon atoms; A is a straight chain or branched chain alkylene radical having 1 - 30 carbon atoms; m has a value in the range of 1 - 15; n has a value in the range of 0 - 6; and R_2 is selected from the group consisting of H, a hydrocarbyl radical having a molecular weight in the range of about 15 to about 10,000, and a homopolymeric or heteropolymeric polyoxyalkylene radical of the formula $R_3 - ((Q)_a(T)_b(Z)_c)_{d^-}$ (III)

[0013] wherein R₃ is H or a hydrocarbyl radical having 1 - 30 carbon atoms, Q, T, and Z are polyoxyalkylene moieties having 1 - 6 carbon atoms, a, b and c each have values ranging from 0 - 30, and d has a value in the range of 1- 50, and (ii) a polybutylamine or polyisobutylamine of the formula

$$R_{11} - CH_2 - N$$
 R_{13}
(IV)

[0014]

where R_{11} is a polybutyl or polyisobutyl radical derived from isobutene and up to 20% by weight of n-butene and R_{12} and R_{13} are identical or different and are each hydrogen, an aliphatic or aromatic hydrocarbon, a primary or secondary, aromatic or aliphatic aminoalkylene radical or polyaminoalkylene radical, a polyoxyalkylene radical or a heteroaryl or heterocyclyl radical, or, together with the nitrogen atom to which they are bonded, form a ring in which further hetero atoms may be present; and (b) a fuel conditioner component comprising: (i) from about 10 to about 70 weight percent, based upon the total weight of the additive, of a polar oxygenated hydrocarbon

having an average molecular weight in the range of about 200 to about 500, an acid number in the range of about 25 to about 175, and a saponification number in the range of about 30 to about 250, and (ii) from about 10 to about 70 weight percent, based upon the total of the additive, of an oxygenated compatibilizing agent preferably having a solubility parameter in the range of about 7.0 to about 14.0 and moderate to strong hydrogencapacity.

- [0015] In one preferred embodiment of the present invention the amino compound of the formula $H = (NH (A)_m)_n Y R_2$ (II)
- [0016] (i) would be made from I and II, II preferably comprising Y = NR₅ and R₅ = U H where U is a polysubstituted, linear or branched, moiety with 1 to 10 carbon units and this preferred embodiment (compound V) further comprises at least one linear or branched carboxylic monoacid or anhydride compound. The compounds I, II and V are necessarily reacted in proportion other than 1:1:1 as described in the U. S. Pat. No. 6,083,287.
- [0017] The fuel conditioner component may additionally comprise a hydrophilic separant such as a glycol monoether. The additive composition may additionally comprise a carrier oil or fluidizer.
- [0018] This invention is also directed to a diesel fuel containing the present invention which may be added with any other additives or added after the addition of any other additives.

DETAILED DESCRIPTION

- [0019] This invention is in one aspect directed to a diesel fuel additive comprising: (a) a detergent component which is selected from the group consisting of (i) the reaction product of a substituted hydrocarbon and an amino compound, (ii) a polybutylamine or polyisobutylamine; and (b) a fuel conditioner component comprising a polar oxygenated hydrocarbon compound and an oxygenated compatibilizing agent.
- [0020] Another aspect of the present invention is directed to a diesel fuel additive comprising (a) a fuel conditioner component comprising a polar oxygenated hydrocarbon compound and an oxygenated compatibilizing agent.
- [0021] If the reaction product detergent component is employed, the substituted hydrocarbon reactant used to prepare the reaction product is of the formula $R_1 X$ (I)
- [0022] wherein R₁ is a hydrocarbyl radical having a molecular weight in the range of about 150 to about 10,000, preferably a polyalkylene radical having a molecular weight in the range of about 400 to about 5000, most preferably a polyalkylene radical having a molecular weight in the range of about 600 to about 1500, and X is selected from the group consisting of halogens, preferably chlorine, succinic anhydride and succinic dibasic acid. in one preferred embodiment, R₁-X is a polyisobutenyl succinic anhydride. In another preferred embodiment, R₁-X is a chloropolyisobutylene, The amino compound reactant used

to prepare the reaction product is of the formula $H = (NH - (A)_m)_n - Y - R_2$ (II)

- [0023] wherein Y is O or NR $_5$, R $_5$ being H or a hydrocarbyl radical having 1 30 carbon atoms, preferably 1 22 carbon atoms; A is a straight chain or branched chain alkylene radical having 1 30, preferably 1 15 carbon atoms; m has a value in the range of 1 15, preferably 1 12; n has a value in the range of 0 6, preferably 0 5; and R $_2$ is selected from the group consisting of H, a hydrocarbyl radical having a molecular weight in the range of about 15 to about 10,000, preferably 15 to about 2000, and a homopolymeric or heteropolymeric polyoxyalkylene radical of the formula $_{3}$ —((Q) $_{a}$ (T) $_{b}$ (Z) $_{c}$) $_{d}$ (III)
- [0024] wherein R₃ is H or a hydrocarbyl radical having 1 30, preferably 1 22 carbon atoms, Q, T, and Z are polyoxyalkylene moieties having 1 6 carbon atoms, a, b, and c each have values ranging from 0 30, and d has a value in the range of 1 50, preferably 1 25.
- [0025] Various preferred embodiments of the amino compound reactant of formula (II) are given in Table 1 below

[0026] Table 1

[0027] 1.A=CH₂, m=2, n=3, Y=NR₅, R₅=H, R₂=H, yields an amino compound reactant of the formula: $_{NH_2}$ — $_{(CH_2)_2}$ — $_{NH}$ — $_{(CH_2)_2}$ — $_{(CH_2)_2}$

[0028] 2.A=CH $_2$, m=3, n=1, Y=NR $_5$, R $_5$ =H, R $_2$ =oleyl radical, yields an amino

compound reactant of the formula: $NH_2 - (CH_2)_3 - NH - oleyl$

- [0029] 3.A=CH $_2$, m=6, n=1, Y=NR $_5$, R $_5$ =H, R $_2$ =H, yields an amino compound reactant of the formula: NH $_2$ —(CH $_2$) $_6$ —NH $_2$
- [0030] 4.A=CH $_2$, m=12, n=1, Y=NR $_5$, R $_5$ =H, R $_2$ =H, yields an amino compound reactant of the formula: NH $_2$ —(CH $_2$) $_{12}$ —NH $_2$

[0031] 5.
$$CH_3$$

 $A = (CH_2)_2 - CH - (CH_2)_3, m=1, n=1, Y=NR_5, R_5=H, R_2=H,$

[0032] yields an amino compound reactant of the

[0033] 6.
$$CH_3$$
 CH_3 CH_3 CH_3 CH_4 CH_5 CH_5 CH_5 CH_5 CH_5 CH_5 CH_5 CH_5 CH_6 CH_7 CH_7 CH_7 CH_7 CH_8 CH_8

[0034] yields an amino compound reactant of the

formula:
$$\begin{matrix} CH_3 & CH_3 \\ I & I \\ NH_2-(CH_2)_2-CH-CH_2-CH-CH_2-NH_2 \end{matrix}$$

[0035] In another preferred embodiment, R₂ is the above-described homopolymeric or heteropolymeric polyoxyalkylene radical of formula (III). As used in this description and in the appended claims, the terms homopolymeric and heteropolymeric refer to polyoxyalkylene compounds, which in the case of homopolymeric compounds contain one recurring polyoxyalkylene moiety, and in the case of heteropolymeric compounds contain more than one recurring polyoxyalkylene moiety, typically having 1-6 carbon atoms, such as

ethylene oxide (EO), propylene oxide (PO) or butylene oxide (BO). Thus, for example, in one embodiment R_2 may be a homopolymeric polyoxyalkylene radical of the formula $R_3 - ((EO))_{d^-}$

- [0036] wherein in formula (III), a = I, b = 0, c = 0, Q = ethylene oxide, and R $_3$ and d are as previously defined. In another embodiment, R $_2$ may be a heteropolymeric polyoxyalkylene radical of the formula $_{R_3}$ —((EO)a(PO)b(BO)c)d-
- [0037] wherein, in formula III, Q = ethylene oxide, T = propylene oxide, Z = butylene oxide, and a, b, c, d and R_3 are as previously described.
- [0038] In yet another preferred embodiment, the above- described amino compound reactant is selected from the group consisting of polyethylene polyamines, polypropylene polyamines and mixtures thereof. In yet another preferred embodiment, such polyamines are monoalkylated.

[0039]

The reaction product component is preferably prepared by reacting the substituted hydrocarbon R₁ X to the amino compound in a mole ratio in the range of 0.2:1 - 20:1, more preferably in the range of 0.5:1 - 10:1. The reaction product component may be prepared under reaction conditions (including e.g. reaction times, temperatures, and reagent proportions) as are well known by those skilled in the art for preparing such amino compound-substituted hydrocarbon reaction products. The method for preparing such reaction products is described, for example, in U.S. Pat. No. 3,172,892 (LeSeur et al.),

U.S. Pat. No. 3,438,757 (Honnen et al.), and U.S. Pat. No. 3,443,918 (Kautsky et al.), all of which are incorporated herein by reference.

[0040]
$$R_{11} - CH_2 - N$$
 R_{13} (IV)

[0041] where R₁₁ is a polybutyl- or polyisobutyl radical derived from isobutene and up to 20% by weight of n-butene, and R₁₂ and R₁₃ are identical or different and are each hydrogen, an aliphatic or aromatic hydrocarbon, a primary or secondary, aromatic or aliphatic aminoalkylene radical or polyaminoalkylene radical, a polyoxyalkylene radical or a heteroaryl or heterocyclyl radical, or, together with the nitrogen atom to which they are bonded, form a ring in which further hetero atoms may be present.

[0042] Compounds of the general formula (IV) and the method of preparation thereof are disclosed, for example, in U.S. Pat. No. 4,832,702 (Kummer et al.), incorporated herein by reference. Compounds of the general formula (IV) are preferably prepared in accordance with the method disclosed in U.S. Pat. No. 4,832,702, wherein an appropriate polybutene or polyisobutene is hydroformylated with a rhodium or cobalt catalyst in the presence of CO and H₂ at from about 80-200°C and CO/H 2 pressures of up to 600 bar, and the oxo product thereby formed is then subjected to a Mannich reaction or amination under hydrogenating conditions, wherein the amination reaction is advantageously carried out at 80 - 200°C and under pressures up to

- 600 bar, preferably 80 300 bar.
- [0043] The fuel conditioner component employed in admixture with the detergent component to produce the additive of this invention may preferably be the fuel conditioner previously disclosed in U.S. Pat. No. 4,753,661 (Nelson et al.), incorporated herein by reference. This fuel conditioner comprises a polar oxygenated hydrocarbon compound and an oxygenated compatibilizing agent.
- [0044] The polar oxygenated hydrocarbon portion of the fuel conditioner signifies various organic mixtures arising from the controlled oxidation of petroleum liquids with air. Often these air oxidations of liquid distillates are carried out at a temperature of from about 100°C to about 150°C with an organo-metallic catalyst, such as esters of manganese, copper, iron, cobalt, nickel or tin, or organic catalysts, such as tertiary butyl peroxide. The result is a melange of polar oxygenated compounds which may be divided into at least three categories: volatile, saponifiable and non-saponifiable.
- [0045] The polar oxygenated compounds preferable for use in the present invention may be characterized in a least three ways, by molecular weight, acid number, and saponification number. It is to be appreciated by those skilled in the art that the terms "molecular weight" and "average molecular weight" are synonymous and are herein used interchangeably. It is to be further appreciated that there are several methods of determining the average molecular weight of an organic material and that different methods will produce different

results for the same material. Chemically these oxidation products are mixtures of acids, hydroxy acids, lactones, eaters, ketones, alcohols, anhydrides, and other oxygenated organic compounds. Those suitable for the present invention are compounds and mixtures with an average molecular weight between about 200 and about 500, with an acid number between about 25 and about 175 (ASTM-D-974), and a saponification number from about 30 to about 250 (ASTM-D-974-52). Preferably the polar oxygenated compounds of the present invention have an acid number from about 50 to about 100 and a saponification number from about 75 to about 200.

[0046]

Suitable compatibilizing agents for use in the fuel conditioner component of the instant invention are organic compounds of moderate solubility parameter and moderate to strong hydrogen-bonding capacity. Solubility parameters, δ , based on cohesive energy density are a fundamental descriptor of an organic solvent giving a measure of its polarity. Simple aliphatic molecules of low polarity have a low δ of about 7.3; highly polar water has a high δ of 23.4. Solubility parameters, however, are just a first approximation to the polarity of an organic solvent. Also important to generalized polarity, and hence solvent power, are dipole moment and hydrogen-bonding capacity. Symmetrical carbon tetrachloride and some aromatics with low gross dipole moment and poor hydrogen-bonding capacity have a solubility parameter of about 8.5. In contrast, methyl propyl ketone has almost the same solubility parameter, 8.7, but quite strong hydrogen-bonding

- capacity and a definite dipole moment. Thus, no one figure of merit alone describes the "polarity" of an organic solvent.
- [0047] For the practice of the present invention a compatibilizing agent preferably having a solubility parameter from about 7.0 to about 14.0 and moderate to strong hydrogen-bonding capacity. Suitable classes of organic solvents are alcohols, ketones, esters, and ethers.

 Preferred compatibilizing agents are straight-chain, branched-chain, and alicyclic alcohols with from six to 14 carbon atoms. Especially preferred compounds for compatibilizing agents are the hexanols, the heptanols, the octanols, the nonyl alcohols, the decanols, and the dodecanols.
- [0048] The fuel conditioner component of this invention may additionally include a hydrophilic separant which decreases the amount of water in the hydrocarbon fuel, thus improving combustion. Suitable separants for practicing the current invention are ethers of glycols or polyglycols, especially monoethers. Monoethers are preferred over diethers in the practice of the present invention.
- [0049] Examples of such compounds which may be used are the monoethers of ethylene glycol, propylene glycol, trimethylene glycol, alphabutylene glycol, 1,3- butanediol, beta-butylene glycol, isobutylene glycol, tetramethylene glycol, hexylene glycol, diethylene glycol, dipropylene glycol, tripropylene glycol, triethylene glycol, tetraethylene glycol, 1,5- pentanediol, 2-methyl-2-ethyl-1,3- propanediol, 2- ethyl-1,3-hexanediol. Some monoethers include

ethylene glycol monophenyl ether, ethylene glycol monomethylether, ethylene glycol monoethyl ether, ethylene glycol mono-(n-butyl) ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol mono-(n-butyl) ether, propylene glycol monomethyl ether, dipropylene glycol monomethyl ether, diethylene glycol monocyclohexylether, ethylene glycol monobenzyl ether, triethylene glycol monophenethyl ether, butylene glycol mono-(p-(nbutoxy) phenyl) ether, trimethylene glycol mono(alkylphenyl) ether, tripropylene glycol monomethyl ether, ethylene glycol mono-isopropyl ether, ethylene glycol monoisobutyl ether, ethylene glycol monohexyl ether, triethylene glycol monobutyl ether, triethylene glycol monomethyl ether, triethylene glycol monoethyl ether, 1-butoxyethoxy-2- propanol, monophenyl ether of polypropylene glycol having an average molecular weight of about 975 to 1075, and monophenyl ether of polypropylene glycol wherein the polyglycol has a average molecular weight of about 400 to 450, monophenyl ether of polypropylene glycol wherein the polypropylene glycol has an average molecular weight of about 975 to 1075. Such compounds are sold commercially under trade names such as Butyl CELLOSOLVE, Ethyl CELLOSOLVE, Hexyl CELLOSOLVE, Methyl CARBITOL, Butyl CARBITOL, DOWANOL Glycol ethers, and the like.

[0050]

The composition of this invention may additionally comprise a suitable amount of a carrier oil or fluidizer selected from the group consisting of petroleum-based oils, mineral oils, polypropylene compounds

having a molecular weight in the range of about 500 to about 3000, polyisobutylene compounds having a molecular weight in the range of about 500 to about 3000, polyoxyalkylene compounds having a molecular weight in the range of about 500 to about 3000, and polybutyl and polyisobutyl alcohols containing polybutyl or polyisobutyl radicals derived from polyisobutene and up to 20% by weight of nbutene, corresponding carboxylates of the polybutyl or polyisobutyl alcohol, and mixtures thereof. Petroleum based oils which may be employed include top cylinder oils as well as both natural and synthetic naphthenic and paraffinic base stock oils of relatively high viscosity, including so-called Solvent Neutral Oils (SNO) such as SNO-500 and SNO-600. Mineral oils which may be employed include so-called "light" mineral oils, i.e. those petroleum, aliphatic or alicyclic fractions having a viscosity less than about 10,000 SUS at 250°C. A mixture of hydrocarbon fractions may also be employed in place of a base stock. The above-described polybutyl and polyisobutyl alcohols include those disclosed in U.S. Pat. No. 4,859,210 (Franz et al.), incorporated herein by reference. As used in this description and in the appended claims, the terms "carrier oil" and "fluidizer" are interchangeable, as will be readily understood by those skilled in the art.

[0051]

Given the presence of the many constituents described above, a wide variety of proportions are suitable for the additive composition of this invention. Below a "Useful Range" and a "Preferred Range" are given

in weight percent, based upon the total weight of the additive composition:

Table 2

•	1 2		
Component	Useful Range	Preferred Range	
Detergent Component	10 - 90	20 - 70	
Polar Oxygenated Compound	10 - 70	20 - 60	
Compatibilizing Agent	10 - 70	15 - 40	
Hydrophilic Separant	0 - 40	0 - 30	

[0052] The additive composition of this invention may be employed in a wide variety of diesel containing fuels for a variety of engines. Preferred diesel fuel compositions for use with the additive composition of this invention are those intended for use in glow plug ignition internal combustion diesel engines. In addition, the diesel fuel composition may additionally comprise other additives typically employed in diesel fuels, such as anti-icing additives, upper cylinder lubricating oils, carburetor detergents, anti-corrosion additives, de-emulsifying agents, odor suppressors, and the like.

[0053] Throughout the specification, examples and claims the following definitions are used.

[0054] Cetane Number (CN) means the measure of ignition quality of diesel fuel based on ignition delay in an engine. The higher the Cetane number is the shorter the ignition delay and the better the ignition quality.

[0055] Cloud Point means the temperature at which a sample of a petroleum

product just shows a cloud or haze of wax crystals when it is cooled under standard test conditions, as defined in ASTM D 2500.

[0056] Pour Point means the lowest temperature at which a petroleum product will just flow when tested under standard conditions, as defined in ASTM D97.

[0057] ASTM means the American Society for Testing and Materials.

[0058] The advantages to diesel fuels include lowering HC emissions, lowering CO emissions, significantly reducing PM emissions thus providing much lower smoke and particulate emissions, accelerating combustion process thereby improving fuel economy and reduced engine noise, reducing cold start and gum formation tendencies, and reduces deposit formation in engines.

[0059] EXAMPLE 1 Cetane Improvement (ASTM D-613)Tests were run on a CFR engine. The table shows the Cetane number increases ranging to a maximum of 5 CN. More specifically a low Cetane of 37.0 has been increased by 1.9 CN.

[0060] CETANE NUMBER IMPROVEMENT

[0061] ASTM D-613

[0062]

(average change)

Fuel	Untreated Fuel	Treated Fuel 500 ppm	Treated Fuel 1000 ppm	
1	37.0 37.0	37.3 37.5 (0.4)	39.0 38.7 (1.9)	
2	42.2 42.3	45.1 45.4 (3.0)	46.3 46.4 (4.1)	
3	44.9		46.8 (1.9)	
4	45.0 45.0		49.6 50.3 (5.0)	
5	52.7		55.2	
Mean Increase		(1.7)	(3.2)	

[0063] (1) = low Cetane diesel fuel

[0064] (5) = low sulfur diesel fuel

[0065] EXAMPLE 2

[0066] Fuel Economy Fuel economy improvements using product of the invention in CI-engines are shown in the table below. Results for identifications 1 through 4 are from dynamometer tests using engines reconditioned prior to testing. Test identifications 5 through 11 are from road or field tests.

[0067]

The data for test identification 1 was obtained with the simulated ECE-15 cycle, the official European legislative procedure used for emission evaluations. All of the identifications are listed in Appendix B. The majority of the additive concentrations for these 11 tests were about 1000 ppm(v). Fuel economy is ranging from 2.2 to 15%:

Fuel No.	Fuel Economy (%)		
4	2.8		
1	14.5		
3	10.7		
3	3.7		
<u> </u>	13.8		
5	3.6		
6	4.1		
7	7.9		
8	15.0		
9	12.7		
11	9.4		

[0068] CI FUEL ECONOMY TEST IDENTIFICATIONS

- [0069] 1.1.6 Liter, 4-cylinder IDI engine; absorption dynamometer; average improvement with Additive concentrations of 500, and 1000 ppm(m).
- [0070] 2.172 KW, 6-cylinder engine; absorption dynamometer; fixed load/speed combination; positive displacement flow meter.
- [0071] 3.7 Liter, 2-stroke DI engine; absorption dynamometer; fixed load/speed combination; positive displacement flow meter.
- [0072] 4.14 Liter, 2-stroke DI engine; absorption dynamometer; fixed load/speed combination; positive displacement flow meter.
- [0073] 5.5.2 Liter engine; 40 mile retraced interstate highway course with onboard flow meter.
- [0074] 6.V-16 Locomotive; 1,000 ppm(v) additive concentration; one hour test at fixed power setting; positive displacement flow meter.
- [0075] 7.5.7 Liter engine; 26 miles retraced interstate highway course with on-board flow meter.

- [0076] 8.Repeat of (6).
- [0077] 9.4-Cylinder motor-generator set with metering tank; 3, 2-hour test runs.
- [0078] 10.V-16 locomotive; 1,000 ppm(v) additive concentration; 24-week tests over retraced course; from fuel records.
- [0079] 11.Same as (10) but with different locomotive and with engine of a different manufacturer.

[0080] EXAMPLE 3

[0081] ENGINE EMISSIONS

- [0082] Cl-engine emissions were determined for two engines on test stands. The first engine was a 4-cylinder, 1.6-liter four-stroke cycle IDI engine. It was tested using a simulated ECE-15 procedure. The fuel was a European, consumer-type, low sulfur fuel. For both the untreated and treated fuel, emission tests were run after a 1-hour break-in following a combustion chamber cleaning and replacement of injectors and valve seats.
- The second engine was a four-cylinder, 4.7-liter (281 in ³) 2-stroke cycle DI engine. It was tested using the SAE J1003, 13-mode test cycle. D-2 Reference Fuel was used untreated for the initial testing after installation of new injectors. Twenty hours of running then was accumulated using the product of the invention treated D-2 Reference Fuel. The 20-hour accumulation cycle consisted of 5 minutes of idle,

40 minutes of 50% load at 26.7Hz (1,600 rpm), 40 minutes of 90% load at 35Hz (2,100 rpm), and 35 minutes of 25% load at 35Hz (2,100 rpm).

[0084] The table below shows that the Additive substantially reduced hydrocarbon emissions and either particulate matter or smoke. The absence of particulate reduction in the 4.7L 2-stroke engine probably reflects 1) the fact that a majority of the 2-stroke particulate matter emissions come from oil consumption and 2) the test procedure. The procedure at Laboratory L-3 did not test the untreated fuel after accumulation of injector deposits.

[0085] PERCENT REDUCTION IN COMPRESSION IGNITION EXHAUST EMISSIONS

TEST PROCEDURE	1.6 L, 4-Stroke IDI ECE-15 SIMULATION			4.7, 2-Stroke DI 13-MODE	
			OVERALL	MAX TORQUE SPEED	MAX LOAD RATED SPEED
Treatment, ppm	500(m)	1000(m)	667(v)	667(v)	667(v)
Particulates	22	39			
Smoke				61	25
HC	13	43	22	23	17
CO	6	22	17	10	27

[0086] In both tests, there is no variation in the NOx emissions.

[0087]